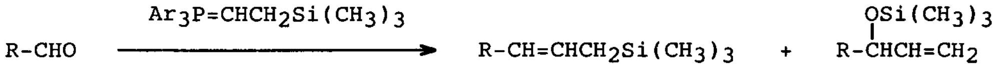
Tetrahedron Letters,Vol.29,No.46,pp 5965-5968,1988   0040-4039/88 $3.00 + .00
Printed in Great Britain   Pergamon Press plc

[2-(TRIMETHYLSILYL)ETHYLIDENE]TRIS(2-METHYLPHENYL)PHOSPHORANE, A MODIFIED SEYFERTH-WITTIG REAGENT FOR THE STEREOSELECTIVE SYNTHESES OF Z-ALLYLTRIMETHYLSILANES

Hideo Iio,* Masahiro Ishii, Masamitsu Tsukamoto, and Takashi Tokoroyama*
Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

Abstract: The Wittig reactions between title β-silylphosphorus ylide and aliphatic aldehydes give selectively Z-allyltrimethylsilanes with minimal formation of vinylation products.

Since its introduction by Seyferth and the modification by Fleming,[1] the Wittig reaction between [2-(trimethylsilyl)ethylidene]triphenylphosphorane (**1**) and aldehydes has been conveniently used for the preparation of allyltrimethylsilanes **3**.[2] Nevertheless, the method has a principal drawback in that it lacks the Z/E-selectivity of the Wittig product **3**; in addition, the formation of silyl group rearranged product **4** is inevitable when the reaction is conducted under more or less diluted conditions.[3] We reported that by modification of the substituents at phosphorus and silicon atoms the Wittig olefination reaction could be thoroughly suppressed[4] and that the reaction of the β-silylphosphorus ylides is useful for highly diastereoselective vinylation of α-substituted aldehydes.[5] In our continuing studies on synthetic application of the modified β-silylphophorus ylide, we have found that the Wittig reaction between [2-(trimethylsilyl)ethylidene]tris(2-methylphenyl)-phosphorane (**2**) and aliphatic aldehydes selectively gave Z-allyltrimethylsilanes **(Z)-3**, which is the subject of this paper.



$$\text{R-CHO} \xrightarrow{\text{Ar}_3\text{P=CHCH}_2\text{Si(CH}_3)_3} \text{R-CH=CHCH}_2\text{Si(CH}_3)_3 + \text{R-}\overset{\text{OSi(CH}_3)_3}{\text{C}}\text{HCH=CH}_2$$

1 : Ar = C_6H_5 **3**   **4**
2 : Ar = $2\text{-}CH_3C_6H_4$

The Wittig reaction of semistabilized ylide such as benzylidenetriphenylphosphorane is known to show low Z/E-selectivity.[6] However, sterically more congested benzylidenetris(2-methylphenyl)phosphorane tends to increase Z-selectivity due to the destabilization of the intermediary oxaphosphetane.[7,8] We anticipated that the replacement of phenyl groups by 2-methylphenyl groups in **1** might improve the Z/E-selectivity of the Wittig product and at the same

Table I. The selectivity in the reaction of β-silylphosphorus ylide with 3-phenylpropanal[a]

Entry	Reaction condition			Product ratio[b]	Isolated yield of **3** (%)
	Ylide	Base	Temp (°C)	(*E*)-**3** : (*Z*)-**3** : **4**	
1	**1**	n-BuLi	0	35 : 100 : 39	62
2	**2**	$(Me_3Si)_2NNa$	-78	0.6 : 100 : 120	29
3	**2**	$(Me_3Si)_2NNa$	-23	1.6 : 100 : 66	21
4	**2**	$(Me_3Si)_2NNa$	0	4.7 : 100 : 22	31
5	**2**	n-BuLi	-78	4.0 : 100 : 15	71
6	**2**	n-BuLi	0	4.3 : 100 : 7.9	82
7	**2**	n-BuLi	25	5.7 : 100 : 4.8	79
8	**2**	n-BuLi	67	7.6 : 100 : 0.7	52

[a] The reactions were carried out in 3 ml THF using 1.0 mmol of 3-phenylpropanal and 1.2 mmol of the ylide prepared from corresponding β-trimethylsilylphosphonium salt and the base specified.

[b] The ratios were determined by capillary GC analysis of crude reaction mixture.

time suppress the formation of rearranged product **4**. The results of the reactions between the β-silylphosphorus ylides and 3-phenylpropanal under various reaction conditions are summarized in Table I. In contrast with the reaction of the ylide **1**, the formation of **4** decreased substantially and better *Z*-selectivity was secured by using **2**. Under the salt-free condition which favors the *Z*-selectivity in unstabilized ylide,[9] the *Z*/*E* ratio of the allylsilane increased, while the formation of vinylation product **4** was enhanced. The ratio among (*E*)-**3**, (*Z*)-**3**, and **4** was also dependent on the reaction temperature (Entry 2∿4). The ylide generated by butyllithium in THF gave **4** in lesser amounts (Entry 5∿8). The reaction at -78 °C gave the highest ratio of **4** due to the relatively slow decomposition of oxaphosphetane to the allylsilane and phosphine oxide. At higher temperature the formation of *E*-allylsilane gradually increased, the result being compatible with the previous observation by Schlosser et al..[9] Allyltrimethylsilanes **3** are easily freed from **4** by chromatography after desilylation of **4**, though the separation of *Z*/*E* isomers of allyltrimethylsilane is usually unattainable. Eventually the reaction at 0 °C with ylide **2** generated by butyllithium (Entry 6) is practically the most suitable for the preparation of *Z*-allyltrimethylsilane with reference to both *Z*-selectivity and yield. The reactions of selected aldehydes under this condition were carried out and are summarized in Table II. The reagent **2** gave

Table II. Syntheses of Z-allyltrimethylsilane with 2 and aldehydes[a]

Entry	Aldehyde	Product ratio[b]			Isolated yield of **3** (%)
		(E)-3	**(Z)-3**	**4**	
1	$PhCH_2CH_2CHO$	4.3	100	7.9	82
2	$CH_3(CH_2)_8CHO$	3.7	100	2.3	91
		(21	100	7)[c]	
3	cyclo-$C_6H_{11}CHO$	3.8	100	3.4	82
		(37	100	15)[c]	
4	$C_6H_5CH(CH_3)CHO$	5.5	100	2.1	88
5	$CH_3CH_2CH_2CH(CH_3)CHO$	2.6	100	<1.0	38[d]
6	PhCHO	27	100	30	76
7	(E)-PhCH=CHCHO	16	100	4.1	76

[a] **A general experimental procedure:** To a stirred suspension of 1.2 mmol of [2-(trimethylsilyl)ethyl]tris(2-methylphenyl)phosphonium iodide[10] in THF (3 ml) was added n-BuLi (1.5 M hexane solution, 1.1 mmol) at 0 °C, and the mixture was stirred for 30 min at room temperature. To the resulting ylide solution was added a solution of 1.0 mmol of aldehyde in THF (1 ml) at 0 °C. Usual workup followed by purification by silica gel chromatography after treatment by 1 M HCl yielded allyltrimethylsilane **3**.[11]

[b] The ratios were determined by capillary GC analysis of the crude reaction mixture.

[c] The ratio in parentheses denotes the selectivity for the reaction carried out using **1** instead of **2** under the same reaction condition.

[d] The relatively moderate yield is due to the volatile nature of the product.

generally Z-allyltrimethylsilane with much higher selectivity (Z/E >94 %) for aliphatic saturated aldehydes than the reaction with **1**. In the reactions with benzaldehyde or cinnamaldehyde substantial amounts of **(E)-3** and **4** formed, which may be attributable to facile reversibility of oxaphosphetane to its precursors ylide and aldehyde in aromatic and unsaturated aldehydes.[8,12] The reaction of aldehydes with an ylide, $(2\text{-}CH_3C_6H_4)_3P{=}C(CH_3)CH_2Si(CH_3)_3$, which has an additional methyl group at α-position of phosphorus atom, did not yield allylsilane but resulted in enolization of aldehyde due to the sterically congested nature of the ylide.

The method for synthesis of Z-allyltrimethylsilane using **2** is highly selective compared with that using **1** reported by Seyferth, and will be applicable to a variety of aliphatic aldehydes.

References and Notes

1. (a) D. Seyferth, K.R. Wurkthorn, R.E. Mammarella, J. Org. Chem. **1977**, 42, 3104. (b) D. Seyferth, K.R. Wursthorn, T.F.O. Lim, and D.J. Sepelak, J. Organomet. Chem. **1979**, 181, 293. (c) I. Fleming and I. Paterson, Synthesis **1979**, 446

2. For other methodologies for the syntheses of allylsilanes, see: (a) Y. Tanigawa, Y. Fuse, and S. Murahashi, Tetrahedron Lett. **1982**, 23, 557. (b) T. Hayashi, K. Kabeta, I. Hamachi, and M. Kumada, Tetrahedron Lett. **1983**, 24, 2865. (c) B.M. Trost, J. Yoshida, and M. Lautens, J. Am. Chem. Soc. **1983**, 105, 4494. (d) H. Urata, H. Suzuki, Y. Moro-oka, and T. Ikawa, Bull. Chem. Soc. Jpn. **1984**, 57, 607. (e) J.G. Smith, S.E. Drozda, S.P. Petraglia, N.R. Quinn, E.M. Rice, B.S. Taylor, and M. Viswanathan, J. Org. Chem. **1984**, 49, 4112. (f) H. Shiragami, T. Kawamoto, K. Utimoto, and H. Nozaki, Tetrahedron Lett. **1986**, 27, 89, (g) E.W. Colvin, "Silicon Reagents in Organic Synthesis", Academic Press, **1988**, pp. 25∿31, and references cited therein.

3. (a) L.R. Hughes, R. Schmid, and W.S. Johnson, Bioorg. Chem. **1979**, 8, 513. (b) S.J. Danishefsky, M.P. DeNinno, G.B. Phillips, R.E. Zelle, and P.A. Lartey, Tetrahedron **1986**, 42, 2809.

4. (a) M. Tsukamoto, H. Iio, and T. Tokoroyama, Tetrahedron Lett. **1985**, 26, 4471. (b) idem, J. Chem. Soc., Chem. Commun. **1986**, 880.

5. (a) H. Iio, T. Mizobuchi, M. Tsukamoto, and T. Tokoroyama, Tetrahedron Lett. **1986**, 27, 6373. (b) H. Iio, T. Mizobuchi, and T. Tokoroyama, Tetrahedron Lett. **1987**, 28, 2379. (c) M. Tsukamoto, H. Iio, and T. Tokoroyama, Tetrahedron Lett. **1987**, 28, 4561.

6. M. Schlosser, Top. Stereochem. **1970**, 5, 1.

7. (a) D.W. Allen, Z. Naturforsch. **1980**, 35b, 1455. (b) idem, J. Chem. Research (S) **1980**, 384.

8. B. Schaub, S. Jeganathan, and M. Schlosser, Chimia **1986**, 40, 246.

9. M. Schlosser, B. Schaub, J. Oliveira-Nero, and S. Jeganathan, Chimia **1986**, 40, 244.

10. This phosphonium salt was obtained in 90 % yield by treating tris(2-methylphenyl)phosphorus methylide [prepared from methyltris(2-methylphenyl)-phosphonium bromide and n-BuLi in THF in situ)] and iodomethyltrimethylsilane in refluxing THF (5 hr). The resulting phosphonium salt was extracted by CH_2Cl_2, and after evaporation of the organic solvent the residue was crystallized from THF-Et_2O. mp. 111-113 °C.

11. Assignment of Z/E isomers of the allyltrimethylsilane is based on 400 MHz ^{1}H NMR data which show that methylene protones adjacent to the trimethylsilyl group are typically at lower field for Z-isomer than for E-isomer.[2e]

12. For the mechanistic consideration of Wittig reaction, see: E. Vedejs and C.F. Marth, J. Am. Chem. Soc. **1988**, 110, 3948, and references cited therein.

(Received in Japan 5 September 1988)